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(54) Method for preparing hydrophobic fumed silica

Verfahren zur Herstellung von hydrophober pyrogener Kieselsäure

Méthode de préparation d'une silice pyrogénique hydrophobe

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- PATENT ABSTRACTS OF JAPAN vol. 1995, no. 01, 28 February 1995 (1995-02-28) & JP 06 298519 A (IDEMITSU KOSAN CO LTD), 25 October 1994 (1994-10-25)





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Description

[0001] The present invention is a method for preparation of hydrophobic fumed silicas which are useful as reinforcing fillers in rubber compositions. The method comprises a first step wherein an aqueous suspension of fumed silica is contacted with an organosilicon compound in the aqueous phase and in the presence of a catalytic amount of an acid to effect hydrophobing of said silica to form an aqueous suspension of a hydrophobic fumed silica. In a preferred method, the first step further comprises the presence of a water-miscible organic solvent which facilitates hydrophobing of said silica with said organosilicon compound. The fumed silica used herein preferably has a BET surface area greater than 50 $m^2/g$. In a second step of this method, the aqueous suspension of hydrophobic fumed silica is contacted with a water-immiscible organic solvent at a solvent to silica weight ratio greater than 0.1:1 to effect separation of a hydrophobic fumed silica from the aqueous phase. In a preferred process, the recovered hydrophobic fumed silica has a surface area within a range of 100 $m^2/g$ to 750 $m^2/g$.

[0002] Although hydrophobic fumed silicas prepared by our claimed method are useful in many applications, such as reinforcing and extending fillers in natural rubbers, thermal insulation and floatation devices, they are particularly useful as reinforcing fillers in silicone rubber compositions. It is well known that silicone rubbers formed from the vulcanization of polydiorganosiloxane fluids or gums generally have low elongation and tensile strength properties. One means for improving these properties involves the incorporation of a reinforcing silica filler, such as fumed silica, into the fluid or gum before curing. However, fumed silica has a tendency to interact with the polydiorganosiloxane fluid or gum to cause a phenomenon typically referred to as "crepe hardening". In the past, a considerable effort has been made to treat the surface of reinforcing silica fillers with organosilanes or organo-siloxanes to make the silica surface hydrophobic. This surface treatment thereby reduces or diminishes the tendency of these compositions to crepe harden and also improves the physical properties of the cured silicone rubber. Known processes for hydrophobing fumed silica, however, contribute significantly to the cost of the fumed silica and therefore less costly methods of treating fumed silica are desired.

[0003] U.S. Patent 3,015,645 teaches making of hydrophobic silica powders by reacting an organosilicon compound, such as dimethyldichlorosilane or trimethyl-methoxysilane, with a silica organogel in the presence of an acidic catalyst to form a hydrophobic silica hydrogel. The hydrophobic silica hydrogel in the aqueous phase is then contacted with a water-immiscible organic solvent to convert the hydrophobic silica hydrogel to a hydrophobic silica organogel which segregates into the organic phase.

[0004] U.S. Patent 4,072,796 describes a method where finely divided hydrophobic silica and silicates are prepared by precipitation of alkali silicate solutions with mineral acids or metal salt solutions and next treated with organohalosilanes. The organohalosilane is a prepolycondensed organohalosilane or a mixture of prepolycondensed organohalosilanes.

[0005] U.S. Patent 5,009,874 also discloses a method for making a hydrophobic precipitated silica useful as a reinforcing filler in silicone elastomers. In a first step, the precipitated silica in aqueous suspension is hydrophobed with an organosilicon compound. In a second step, a water-immiscible organic solvent is added to effect separation of the hydrophobic precipitated silica from the aqueous phase. The water immiscible organic solvent is normally added to the process at a volume(L) to weight (Kg) ratio of silica of from 1 to 5 and preferably from 1.5 to 4.5.

[0006] British Specification 1,110,331 claims the hydrophobing of an aqueous suspension of fumed silica having a BET surface area of 50 $m^2/g$ with a alkyl halogen silane and the subsequent flocculation in a water-immiscible organic liquid, in quantities of from 0.01 to 1X based on the entire weight of the suspension. In the example, this reference details the addition of 3 ml of toluene to an aqueous suspension comprising 300 g of hydrophobed silica that provides for a solvent to silica ratio of 0.01:1. This reference does not suggest or teach the use of a polar organic solvent to facilitate hydrophobing of the fumed silica.

[0007] The present invention provides a method for preparing a hydrophobic fumed silica. Our method comprises: (A) contacting an aqueous suspension of a fumed silica with (1) a catalytic amount of an acid and (2) an organosilicon compound selected from the group consisting of organosilanes described by formulae $R^1_aH_bSiX_{4-a-b}$ (1), $R^2_nSiO_{(4-n)/2}$ (2) and $(R^3_3Si)_2NH$ (3) where each $R^1$ is an independently selected hydrocarbon radical comprising 1 to 12 carbon atoms, each $R^2$ is independently selected from the group consisting of hydrogen or chlorine atoms and hydroxy or hydrocarbon radicals comprising 1 to 12 carbon atoms, with the proviso that at least 50 mole percent of the $R^2$ substituents are hydrocarbon radicals, each $R^3$ is independently selected from the group consisting of chlorine, hydroxy and hydrocarbon radicals comprising 1 to 12 carbon atoms, with the proviso that at least 50 mole percent of the $R^3$ substituents are hydrocarbon radicals, each X is independently selected from the group consisting of halogen atoms, alkoxy radicals comprising 1 to 12 carbon atoms and acyloxy radicals comprising 1 to 12 carbon atoms; a=1, 2 or 3; b=0 or 1; a+b=1, 2 or 3, with the proviso that when b=1 then a+b=2 or 3; and n is an integer from 2 to 3 inclusive, to form an aqueous suspension of a hydrophobic fumed silica; and (B) contacting the aqueous suspension of the hydrophobic fumed silica of (A) with a water-immiscible organic solvent at a solvent to silica weight ratio greater than 0.1:1 to thereby effect separation of a hydrophobic fumed silica from the aqueous suspension by way of the formation of an

aggregation of hydrophobic silica particles, incorporating water-immiscible organic solvent, in a water-immiscible organic solvent phase.

[0008] In step (A) of our method, an aqueous suspension of a fumed silica is hydrophobed with an organosilicon compound. By "fumed silica", we mean those high-surface area silicas prepared by a pyrogenic process. Such pyrogenic processes include the vapor-phase hydrolysis of halosilanes, such as trichlorosilane and tetrachlorosilane in an electric arc furnace. Other methods include vaporization of $SiO_2$, vaporization and oxidation of Si and high temperature oxidation and hydrolysis of silicon compounds such as silicate esters. Preferred is a fumed silica prepared by the vapor-phase hydrolysis of a halosilane.

[0009] The BET surface area of the fumed silica used in the present method is preferably greater than 50 $m^2/g$ to 1000 $m^2/g$. More preferred is a BET surface area of 75 $m^2/g$ to 1000 $m^2/g$. A most preferred fumed silica, particularly when it is to be used as a reinforcing filler in rubber compositions, has a BET surface area within a range of 100 $m^2/g$ to 750 $m^2/g$.

[0010] The fumed silica is conveniently added to step (A) of our method as an aqueous suspension. The concentration of fumed silica in the aqueous suspension is not critical and it is normally within a range of 5 to 90 weight percent. Preferred is a concentration of fumed silica in the aqueous suspension within a range of 10 to 50 weight percent. Most preferred is a concentration of 10 to 30 weight percent.

[0011] In step (A) of our method, the aqueous suspension of fumed silica is contacted with one or more of the organosilicon compounds described by formulas (1), (2) and (3) in the presence of a catalytic amount of an acid. The acid catalyst is, for example, a mineral acid such as hydrochloric, hydroiodic, sulfuric, nitric, benzene sulfonic and phosphoric acid. When the organosilicon compound is, for example, a chlorosilane, the catalytic amount of acid may also be generated in situ by either hydrolysis of the chlorosilane or by the reaction of the chlorosilane directly with the hydroxyl groups of the fumed silica. In our step (A), it is only necessary that the acid be present in an amount sufficient to effect reaction of the organosilicon compound with the fumed silica. It is also preferred that the acid catalyst provide a pH of 6 or less. More preferred is a pH of 3 or less.

[0012] The temperature at which step (A) is conducted is not critical and is typically within a range of 20°C. to 250°C. Generally, it is preferred that a temperature within a range of 30°C. to 150°C. be employed. Step (A) can also be conducted at the reflux temperature of the polar organic solvent or the water-immiscible organic solvent when present.

[0013] During step (A), it is preferred to add a water-miscible organic solvent in an amount sufficient to facilitate hydrophobing of the fumed silica with the organosilicon compound.

[0014] The method of this preferred embodiment comprises: (A) contacting an aqueous suspension of a fumed silica having a BET surface area of greater than 50 $m^2/g$ and a water-miscible organic solvent in an amount sufficient to facilitate subsequent reaction of said fumed silica with an organosilicon compound with (1) a catalytic amount of an acid and (2) an organosilicon compound selected from the group consisting of organosilanes described by formulae $R^1_aH_bSiX_{4-a-b}$ (1), $R^2_nSiO_{(4-n)/2}$ (2) and $(R^3_3Si)_2NH$ (3), where each $R^1$ is an independently selected hydrocarbon radical comprising 1 to 12 carbon atoms, each $R^2$ is independently selected from the group consisting of hydrogen or chlorine atoms and hydroxy or hydrocarbon radicals comprising 1 to 12 carbon atoms, with the proviso that at least 50 mole percent of the $R^2$ substituents are hydrocarbon radicals, each $R^3$ is independently selected from the group consisting of chlorine, hydroxy and hydrocarbon radicals comprising 1 to 12 carbon atoms, with the proviso that at least 50 mole percent of the $R^3$ substituents are hydrocarbon radicals, each X is independently selected from the group consisting of halogen atoms, alkoxy radicals comprising 1 to 12 carbon atoms and acyloxy radicals comprising 1 to 12 carbon atoms, a=1, 2 or 3; b=0 or 1; a+b=1, 2 or 3, with the proviso that when b=1 then a+b=2 or 3; and n is an integer from 2 to 3 inclusive to form an aqueous suspension of a hydrophobic fumed silica and (B) contacting the aqueous suspension of the hydrophobic fumed silica of (A) with a water-immiscible organic solvent at a solvent to silica weight ratio greater than 0.1:1 to thereby effect separation of a hydrophobic fumed silica from the aqueous suspension.

[0015] Preferred is when the water-miscible organic solvent comprises at least 10 weight percent of the aqueous suspension comprising the fumed silica. Even more preferred is when said organic solvent comprises 15 to 50 weight percent of the aqueous suspension. Most preferred is when the water-miscible organic solvent is 20 to 30 weight percent of the aqueous suspension. Suitable water-miscible solvents include, for example, alcohols such as ethanol, isopropanol and tetrahydrofuran. Isopropanol is a preferred water-miscible organic solvent for use in our claimed method.

[0016] During step (A), it may also be desirable to add a surfactant to facilitate the reaction of the organosilicon compound with the fumed silica. This surfactant may be added in the presence, or absence, of any water-miscible or water-immiscible organic solvents that are added to our method. Suitable surfactants include, for example, anionic surfactants such as dodecylbenzene sulfonic acid; nonionic surfactants such as polyoxyethylene(23)lauryl ether and $(Me_3SiO)_2MeSi(CH_2)_3(OCH_2CH_2)_7OMe$ where Me is methyl and cationic surfactants such as N-alkyltrimethyl ammonium chloride.

[0017] In step (A), the fumed silica is reacted with one or more organosilicon compounds described by formulas (1), (2) or (3). In formula (1) each $R^1$ is an independently selected hydrocarbon radical comprising 1 to 12 carbon atoms.

$R^1$ can be either a saturated or unsaturated monovalent hydrocarbon radical. $R^1$ can also be a substituted or non-substituted monovalent hydrocarbon radical. $R^1$ is represented, for example, by alkyl radicals such as methyl, ethyl, propyl, t-butyl, hexyl, heptyl, octyl, decyl and dodecyl; alkenyl radicals such as vinyl, allyl and hexenyl; substituted alkyl radicals such as chloromethyl, 3,3,3-trifluoropropyl and 6-chlorohexyl; and aryl radicals such as phenyl, naphthyl and tolyl. $R^1$ can further be an organofunctional hydrocarbon radical comprising 1 to 12 carbon atoms where, for example, the functionality is mercapto, disulfide, polysulfide, amino, carboxylic acid carbinol ester or amido. A preferred organofunctional hydrocarbon radical is one having disulfide or polysulfide functionality.

[0018] In formula (1), each X is independently selected from the group consisting of halogen atoms, alkoxy radicals comprising 1 to 12 carbon atoms and acyloxy radicals comprising 1 to 12 carbon atoms. When X is a halogen, it is preferred that the halogen be chlorine. When X is an alkoxy radical, X is, for example, methoxy, ethoxy and propoxy. When X is an acyloxy radical, X is, for example, acetoxy. Preferred is where each X is selected from the group consisting of chlorine atoms and methoxy groups.

[0019] In formula (2), each $R^2$ is independently selected from the group consisting of hydrogen atom or chlorine atom and hydroxy; or hydrocarbon radicals comprising 1 to 12 carbon atoms, with the proviso that at least 50 mole percent of the $R^2$ substituents are hydrocarbon radicals. $R^2$ is also the same as $R^1$ described above. The organosiloxanes described by formula (2) can be, for example, linear or cyclic in structure. The viscosity of the organosiloxanes described by formula (2) is not limiting and ranges from that of a fluid to a gum. Generally, higher molecular weight organosiloxanes will be cleaved by the acidic conditions of the present method allowing them to react with the fumed silica.

[0020] In formula (3), each $R^3$ is independently selected from the group consisting of chlorine atom, hydroxy group and hydrocarbon radicals comprising 1 to 12 carbon atoms with the proviso that at least 50 percent of the $R^3$ substituents are hydrocarbon radicals. When $R^3$ is a hydrocarbon radical, $R^3$ can be the same as those hydrocarbon radicals described for $R^1$. Preferred is when $R^3$ is methyl.

[0021] Examples of useful organosilicon compounds include diethyldichlorosilane, allylmethyldichlorosilane, methylphenyldichlorosilane, phenylethyldiethoxysilane, 3,3,3-trifluoropropylmethyldichlorosilane, trimethylbutoxysilane, symdiphenyltetramethyldisiloxane, trivinyltrimethylcyclotrisiloxane, octamethylcyclotetra-siloxane, hexaethyldisiloxane, pentylmethyldichlorosilane, divinyldipropoxysilane, vinyldimethylchlorosilane, vinylmethyldichlorosilane, vinyldimethylmethoxysilane, trimethylchlorosilane, hexamethyldisiloxane, hexenylmethyldichlorosilane, hexenyldimethylchlorosilane, dimethylchlorosilane, dimethyldichlorosilane, mercaptopropylmethyldimethoxysilane, bis{3-(triethoxysilyl)propyl}-tetrasulfide, polydimethylcyclosiloxanes comprising 3 to 20 dimethylsiloxy units and preferably 3 to 7 dimethylsiloxy units; and trimethylsiloxy, dimethylchlorosiloxy or hydroxydi-methylsiloxy endblocked polydimethylsiloxane polymers having a viscosity within a range of 1 mPa·s to 1,000 mPa·s at 25°C.

[0022] The amount of organosilicon compound added to our method is that sufficient to adequately hydrophobe the fumed silica to provide a hydrophobic fumed silica suitable for its intended use. Generally, the organosilicon compound is added to the claimed method in an amount such that there is at least 0.04 organosilyl unit per $SiO_2$ unit in the fumed silica. The upper limit of the amount of organosilicon compound added to our process is not critical since any amount in excess of the amount required to saturate the hydroxyl groups of the fumed silica will act as a solvent for the claimed method.

[0023] In step (B), a water-immiscible organic solvent is added at a solvent to silica weight ratio greater than 0.1:1 to effect separation of a hydrophobic fumed silica from the aqueous suspension. In a preferred method, step (A) of our method is conducted and then step (B) is subsequently conducted. However, in the present method, the water-immiscible organic solvent can be added prior to, simultaneously with, or subsequent to the addition of the organosilicon compound of step (A). In these first two situations, the conversion of the fumed silica to a hydrophobic fumed silica is accompanied by a phase separation in which the hydrophobic fumed silica separates into the solvent phase.

[0024] For purposes of this invention, any organic solvent immiscible with water can be employed. Suitable water-immiscible organic solvents include low molecular weight siloxanes such as hexamethyldisiloxane, octamethylcyclotetrasiloxane, diphenyltetramethyldisiloxane and trimethylsiloxy endblocked polydimethylsiloxane fluids. When a siloxane is employed as a solvent, it may serve both as a solvent and as a reactant with the fumed silica. In addition, suitable water-immiscible organic solvents include aromatic hydrocarbons such as toluene and xylene; heptane, hexane and other aliphatic hydrocarbon solvents; cycloalkanes such as cyclohexane; ethers such as diethylether and dibutylether; halohydrocarbon solvents such as methylene chloride, chloroform, ethylene chloride and chlorobenzene; and ketones such as methylisobutylketone.

[0025] The amount of water-immiscible organic solvent added to our claimed method provides a solvent to silica weight ratio greater than 0.1:1. Preferred is a solvent to silica weight ratio of 0.1:1 to 10:1. Most preferred is a solvent to silica weight ratio of 1:1 to 5:1. The upper limit for the amount of water-immiscible solvent added to our method is limited only by economic considerations, such as solvent cost, solvent recovery or disposal expense and equipment capacity. However, at solvent to silica ratios greater than 5:1, a portion of the hydrophobic fumed silica may emulsify making complete recovery of the hydrophobic fumed silica difficult. In the present method, the solvent to silica ratio is such that flocculation of the hydrophobic fumed silica occurs. By "flocculation", we mean that an aggregation of treated

silica particles incorporating the water-immiscible organic solvent suspends as aggregates in the organic solvent phase, thereby creating a distinct boundary between the silica/solvent phase and aqueous phase with minimal or no emulsion layer is formed. Typically, such flocculation is achieved by a solvent to silica ratio within the preferred range of 1:1 to 5:1.

[0026] It is preferred that the water-immiscible organic solvent have a boiling point of 250°C. or below to facilitate its removal from the hydrophobic fumed silica. However, the boiling point of the water-immiscible organic solvent is not critical since the solvent may also be removed from the hydrophobic silica by filtration, centrifuging or other suitable means.

[0027] In step (B), the water-immiscible organic solvent is added to our method thereby effecting separation of the hydrophobic fumed silica from the aqueous suspension. The hydrophobic fumed silica is recovered in the solvent phase to provide a product which may be used, if desired, without further treatment. Alternatively, the hydrophobic fumed silica may be washed to reduce contaminates. The hydrophobic fumed silica may also be recovered from the solvent, dried and further treated by such methods as heating.

Example 1

[0028] Fumed silica was hydrophobed with hexamethyldisiloxane. Into a 500 ml flask were added 20 g of fumed silica (Cabot™ MS75D, BET surface area of 275 $m^2/g$, Cabot Corporation, Tuscola, IL), 200 g of distilled water and 90 g of isopropanol to form a suspension. With constant stirring, 0.5 g of $FeCl_3$, 1 g of concentrated HCl and 50 g of hexamethyldisiloxane were added to this suspension. The suspension was refluxed for 30 minutes with constant stirring. After cooling, the suspension was transferred to a separatory funnel containing 400 ml of toluene and 600 ml of water. Upon agitation, the content of the separatory funnel formed a clear upper layer comprising a silica/solvent phase and a lower aqueous phase. Thereafter, 300 ml of distilled water was trapped as emulsion between the upper and lower phases. The silica/solvent phase was recovered and washed three times with 100 ml aliquots of distilled water. Residual water was removed by azeotropic distillation and the hydrophobic fumed silica was isolated by filtration. Residual solvent was removed from the hydrophobic fumed silica by heating at 130°C. for 24 hours. The dried hydrophobic fumed silica was determined to comprise 2.95 weight percent of carbon by CHN analysis using a Perkin™ Elmer Model 2400, CHN Elemental Analyzer (Perkin Elmer Corporation, Norwalk, CT).

Example 2

[0029] Fumed silica was hydrophobed with dimethyldichlorosilane. Into a 100 ml flask were added 25 g of fumed silica (Cabot™ MS75D), 281 g of distilled water and 90 g of isopropanol to form a suspension. With stirring, 11 g of dimethyldichlorosilane were added to the mixture over a 3 minute period. The suspension was heated to reflux for 30 minutes with constant stirring. After cooling, 300 ml of toluene were added to the flask and the flask content stirred to effect transfer of the hydrophobic fumed silica into the toluene phase. The toluene phase was recovered and washed three times with 300 ml aliquots of distilled water with gentle mixing to avoid formation of an emulsion phase. Residual water was removed by azeotropic distillation and the hydrophobic fumed silica separated from the toluene by distillation. Residual solvent was removed from the hydrophobic fumed silica by heating at 130°C. for 24 hours. The dried hydrophobic fumed silica was determined to comprise 5.37 weight percent of carbon by CHN analysis as above.

Example 3

[0030] Fumed silica was hydrophobed with hexamethyldisiloxane. Into a 5 L flask were added 180 g of fumed silica (Cabot™ MS75D), 803 g of distilled water, 179 g of concentrated HCl, 316 g of isopropanol and 150 g of hexamethyldisiloxane. The resulting suspension was refluxed for 1 hour. After cooling the suspension, toluene was slowly added to the suspension and the consistency of the suspension was visually observed as a function of added toluene. After the addition of 154 g of toluene, a noticeable drop in viscosity of the suspension was noted. When a total of 174 g of toluene had been added, the suspension began to flocculate forming dough-like clumps in the suspending aqueous phase. Significant clumping was visible after a total addition of 188 g of toluene. After a total addition of 205 g of toluene, the clumps began to disappear forming a uniform phase on the surface of the aqueous phase. Further solvent addition reduced the viscosity of the silica/solvent slurry to yield a uniform suspension of the hydrophobic fumed silica.

Example 4

[0031] Fumed silica was hydrophobed with hexamethyldisiloxane, with excess hexamethyldisiloxane serving as a water-immiscible organic solvent. Into a 5 L flask were added 180 g of fumed silica (Cabot™ MS75D), 821 g of distilled water, 200 g of concentrated HCl, 336 g of isopropanol and 350 g of hexamethyldisiloxane to form a suspension. The suspension was heated to reflux along with stirring. As the suspension was refluxed, the viscosity began to rise and

as the fumed silica was hydrophobed, silica flocculation began to occur in the excess hexamethyldisiloxane. After cooling, the mixture was allowed to separate into two phases of an organic phase separated from an aqueous phase. 1.5 L of distilled water were next added to the organic phase and stirring continued for 30 minutes. The organic phase was washed with 1.5 L of distilled water, containing 1.5 g of sodium bicarbonate and then washed with three 1.5 L aliquots of distilled water. During these washing steps, a further 242 g of hexamethyldisiloxane were added to the hydrophobic fumed silica flocculate to maintain a soft consistency. The flocculated hydrophobic fumed silica was separated from the hexamethyldisiloxane by evaporation at room temperature. The hydrophobic fumed silica was dried in an oven at 130°C. for 24 hours. The dried hydrophobic fumed silica was determined to comprise 1.64 weight percent of carbon by the same CHN analysis.

Example 5

[0032] Fumed silica was hydrophobed with octamethylcyclotetrasiloxane (D4) and flocculated with hexamethyldisiloxane serving as a water-immiscible organic solvent. Into a 5 L flask were added 180 g of fumed silica (Cabot™ MS75D), 820 g of distilled water, 180 g of concentrated HCl, 333 g of isopropanol and 50 g of octamethylcyclotetrasiloxane to form a suspension. The suspension was heated to reflux for 30 minutes, with stirring. After cooling, 700 ml of hexamethyldisiloxane were added to the suspension to flocculate the hydrophobed fumed silica. The aqueous phase was removed by decantation. 1.5 L of distilled water were then added to the organic phase and stirring continued for 30 minutes. The organic phase was washed with 1.5 L of distilled water containing 1.5 g of sodium bicarbonate and then washed with three 1.5 L aliquots of distilled water. The flocculated hydrophobic fumed silica was separated from the hexamethyldisiloxane by evaporation at room temperature. The hydrophobic fumed silica was dried in an oven at 130°C. for 24 hours and the weight percent of carbon (Wt. % C) as determined by CHN analysis, as above, was reported in Table 1. This procedure was repeated with octamethylcyclotetrasiloxane levels of 25, 90 and 130 g, with the reagent levels and flocculation solvent quantities used also recorded in Table 1. The weight percent of carbon of the dried hydrophobic fumed silica, as determined by CHN analysis, was also reported in Table 1.

Table 1

Treatment of Fumed Silica With Octamethylcyclotetrasiloxane

| Treating Agent | Wt. Treating Agent (g) | Silica (g) | Water (g) | HCl (g) | IPA | Floc. Solvent | Floc. Solvent (g) | Wt. %C |
|---|---|---|---|---|---|---|---|---|
| D4 | 25 | 180 | 823 | 179 | 333 | HMDS* | 722 | 3.56 |
| D4 | 50 | 180 | 820 | 180 | 333 | HMDS | 700 | 6.38 |
| D4 | 90 | 180 | 824 | 181 | 333 | HMDS | 583 | 9.28 |
| D4 | 130 | 180 | 823 | 181 | 333 | HMDS | 426 | 9.53 |

*HMDS - Hexamethyldisiloxane

Example 6

[0033] Fumed silica was hydrophobed with dimethyldichlorosilane and flocculated with various water-immiscible organic solvents. Into a 5 L flask were added 180 g of fumed silica (Cabot™ MS75D), 1000 g of distilled water and 333 g of isopropanol to form a suspension. The suspension was refluxed for 30 minutes. After cooling, this suspension to room temperature, hexamethyldisiloxane was added to flocculate the hydrophobic fumed silica. The aqueous phase was removed by decantation and the organic phase was washed with 1.5 L of distilled water by stirring for 30 minutes. The organic phase was neutralized with 1.5 L of water containing 1.5 g of sodium bicarbonate and then washed with three 1.5 L aliquots of distilled water. During the washing step, additional hexamethyldisiloxane was added to maintain a soft flocculate consistency. The flocculated hydrophobic fumed silica was then separated from the hexamethyldisi-

loxane by evaporation at room temperature. The hydrophobic fumed silica was dried in an oven at 130°C. for 24 hours and the weight percent of carbon as determined by CHN analysis was reported in Table 2. This procedure was repeated with the dimethyldichlorosilane levels reported in Table 2 and with the reagent levels and flocculation solvent quantities reported in Table 2. The weight percent of carbon as determined by CHN analysis is also reported in Table 2.

Table 2

| Treatment of Fumed Silica With Dimethyldichlorosilane | | | |
|---|---|---|---|
| Wt. Treating Agent (g) | Floc. Solvent | Floc. Solvent (g) | Wt. % C |
| 35 | HMDS* | 663 | 3.31 |
| 51 | HMDS | 570 | 3.94 |
| 60 | Hexane | 900 | 4.22 |
| 70 | Hexane | 586 | 5.19 |
| 76 | HMDS | 482 | 5.11 |
| 80 | Hexane | 570 | 5.66 |
| 90 | Hexane | 429 | 7.18 |
| 100 | HMDS | 400 | 6.17 |
| 135 | HMDS | 428 | 7.87 |
| 183 | HMDS | 436 | 9.27 |

*Hexamethyldisiloxane

Example 7

[0034] Fumed silica was hydrophobed with a mixture of hexenyldimethylchlorosilane and dimethyldichlorosilane. Into a 100 ml flask were added 25 g of fumed silica (Cabot™ MS75D), 289 g of distilled water and 90 g of isopropanol to form a suspension. A mixture comprising 8 g of dimethyldichlorosilane and 2 g of hexenyldimethylchlorosilane was added drop-wise to this suspension over a 3 minute period. With stirring, the suspension was heated to reflux for 30 minutes and then cooled. To the cooled suspension was then added cyclohexane to effect flocculation of the hydrophobic fumed silica. After addition of 76 g of cyclohexane, a flocculate having an average particle size of 0.5 mm was obtained. After further addition of 76 g of cyclohexane, the flocculate had an average particle size of 2 mm. Subsequent additions of cyclohexane resulted in mass clumping of the flocculate. After addition of 90 g of cyclohexane, the aqueous phase was removed by decantation and the organic phase containing the flocculate was washed with 500 ml of distilled water. Additional washing then occurred with 500 ml of distilled water containing 0.5 g of sodium bicarbonate. The flocculate was next washed with two addition 500 ml aliquots of distilled water and then air dried. The air dried flocculate, comprising the hydrophobic fumed silica, was thereafter dried in an oven at 130°C. for 24 hours. The dried hydrophobic fumed silica was determined to comprise 3.83 weight percent of carbon by CHN analysis as above.

Example 8

[0035] Fumed silica was hydrophobed with chlorine end-blocked polydimethylsiloxane oligomers. Into a 5 L flask were placed 180 g of fumed silica (Cabot™ MS75D), 1000 g of distilled water and 333 g of isopropanol to form a suspension. Then, 75 g of chlorine end-blocked polydimethyldisiloxane having an average degree of polymerization of 12 were added to the suspension. The suspension was heated to 60°C. and an additional 108 g of the chlorine end-blocked polydimethyldisiloxane were added. The suspension was heated to 75°C. for 15 minutes and then cooled. To the suspension were added 474 g of hexamethyldisiloxane to effect flocculation of the hydrophobic fumed silica. The aqueous phase was removed and the solvent phase containing the flocculated hydrophobic fumed silica was washed twice with 1500 g of distilled water. The solvent phase containing the hydrophobic fumed silica flocculate was allowed to air dry and the hydrophobic fumed silica further dried in an oven at 150°C. for 24 hours.

Example 9

[0036] Fumed silica was contacted with dimethyldichlorosilane in the absence of a water miscible solvent. Into a 5 L flask were added 150 g of fumed silica (Cabot™ MS75D) and 1500 g of water to form a suspension. The suspension

was heated to 70°C. and then 60 g of dimethyldichlorosilane were added over a 10 minute period with stirring. The suspension was cooled to room temperature and 500 g of toluene were slowly added to the suspension. No flocculation of the fumed silica was observed. The suspension was air dried. The dried fumed silica was determined to comprise 4.1 weight percent of carbon by the same CHN analysis.

Example 10

[0037] Fumed silica was hydrophobed with methyltrichlorosilane and hexamethyldisilazane. Into a 5 L flask were added 110 g of fumed silica (Cabot™ MS75D), 610 g of water and 204 g of isopropanol to form a suspension. Then 118 g of methyltrichlorosilane were added drop-wise to the suspension over a three minute period. With stirring, the suspension was heated to reflux for 30 minutes and then cooled. To the cooled suspension were added 360 g of hexane to effect partial flocculation of the silica. Complete flocculation of the silica was achieved by addition of 30 g. of hexamethyldisilazane and a further addition of 40 g of cyclohexane. Following the second addition of cyclohexane, the aqueous phase was removed by decantation and the organic phase containing the flocculate was washed with 500 ml of distilled water followed by washing with 500 ml of distilled water containing 0.5 g of sodium bicarbonate. The flocculate was then washed with two additional 500 ml aliquots of distilled water and air dried. The air dried flocculate comprising the hydrophobic fumed silica was further dried in an oven at 130°C. for 24 hours. The dried hydrophobic fumed silica was determined to comprise 6.09 weight percent of carbon by CHN analysis.

## Claims

1. A method for preparing a hydrophobic fumed silica comprising (A) contacting an aqueous suspension of a fumed silica with (1) a catalytic amount of an acid and (2) an organosilicon compound selected from the group consisting of organosilanes described by formulae $R^1_aH_bSiX_{4-a-b}$ (1), $R^2_nSiO_{(4-n)/2}$ (2) and $(R^3_3Si)_2NH$ (3) where each $R^1$ is an independently selected hydrocarbon radical comprising 1 to 12 carbon atoms, each $R^2$ is independently selected from the group consisting of hydrogen or chlorine atoms and hydroxy or hydrocarbon radicals comprising 1 to 12 carbon atoms, with the proviso that at least 50 mole percent of the $R^2$ substituents are hydrocarbon radicals, each $R^3$ is independently selected from the group consisting of chlorine, hydroxy and hydrocarbon radicals comprising 1 to 12 carbon atoms, with the proviso that at least 50 mole percent of the $R^3$ substituents are hydrocarbon radicals, each X is independently selected from the group consisting of halogen atoms, alkoxy radicals comprising 1 to 12 carbon atoms, and acyloxy radicals comprising 1 to 12 carbon atoms, a=1, 2 or 3; b=0 or 1; a+b=1, 2 or 3, with the proviso that when b=1 then a+b=2 or 3; and n is an integer from 2 to 3 inclusive, to form an aqueous suspension of a hydrophobic fumed silica; and (B) contacting the aqueous suspension of the hydrophobic fumed silica of (A) with a water-immiscible organic solvent at a solvent to silica weight ratio greater than 0.1:1 to thereby effect separation of the hydrophobic fumed silica from the aqueous suspension by way of the formation of an aggregation of hydrophobic silica particles, incorporating water-immiscible organic solvent, in a water-immiscible organic solvent phase.

2. A method according to claim 1 where the fumed silica has a BET surface area greater than 50 $m^2/g$.

3. A method according to claims 1 or 2 where the aqueous suspension of step (A) further comprises a water-miscible organic solvent in an amount sufficient to facilitate reacting of the fumed silica with the organosilicon compound.

4. A method according to any of claims 1 to 3 where the fumed silica is prepared by the vapor-phase hydrolysis of a halosilane.

5. A method according to any of claims 1 to 4 where the concentration of the fumed silica in the aqueous suspension is within a range of 5 to 90 weight percent.

6. A method according to any of claims 1 to 5 where the catalytic amount of the acid provides for a pH of 6 or less during the contacting of step (A).

7. A method according to any of claims 1 to 6 where the contacting of step (A) is effected at a temperature within a range of 20°C. to 250°C.

8. A method according to any of claims 3 to 7 where the water-miscible organic solvent comprises at least 10 weight percent of the aqueous suspension.

9. A method according to any of claims 1 to 8 where the contacting of step (A) is conducted in the presence of a surfactant which facilitates reaction of the organosilicon compound with the fumed silica.

10. A method according to any of claims 1 to 9 where the organosilicon compound is added in an amount such that there is at least 0.04 organosilyl unit per $SiO_2$ unit in the fumed silica.

Patentansprüche

1. Verfahren zur Herstellung einer hydrophoben pyrogenen Kieselsäure, umfassend (A) In-Berührung-Bringen einer wässrigen Suspension einer pyrogenen Kieselsäure mit (1) einer katalytischen Menge einer Säure und (2) einer Organosiliciumverbindung, ausgewählt aus der Gruppe bestehend aus Organosilanen, beschrieben durch Formeln $R^1_aH_bSiX_{4-a-b}$ (1), $R^2_nSiO_{(4-n)/2}$ (2) und $(R^3_3Si)_2NH$ (3), worin jedes $R^1$ unabhängig voneinander ausgewählt ist aus Kohlenwasserstoffresten mit 1 bis 12 Kohlenstoffatomen, jedes $R^2$ unabhängig voneinander ausgewählt ist aus der Gruppe bestehend aus Wasserstoff- oder Chloratomen und Hydroxy- oder Kohlenwasserstoffresten mit 1 bis 12 Kohlenstoffatomen, unter der Voraussetzung, dass mindestens 50 Mol-% der $R^2$-Substituenten Kohlenwasserstoffreste sind, jedes $R^3$ unabhängig voneinander ausgewählt ist aus der Gruppe bestehend aus Chlor, Hydroxy- oder Kohlenwasserstoffresten mit 1 bis 12 Kohlenstoffatomen, unter der Voraussetzung, dass mindestens 50 Mol-% der $R^3$-Substituenten Kohlenwasserstoffreste sind, jedes X unabhängig voneinander ausgewählt ist aus der Gruppe bestehend aus Halogenatomen, Alkoxyresten mit 1 bis 12 Kohlenstoffatomen und Acyloxyresten mit 1 bis 12 Kohlenstoffatomen, a gleich 1, 2 oder 3 ist; b gleich 0 oder 1 ist; a+b gleich 1, 2 oder 3 ist, unter der Voraussetzung, dass, wenn b gleich 1 ist, dann a+b gleich 2 oder 3 ist, und n eine ganze Zahl von 2 bis 3 einschließlich ist, um eine wässrige Suspension einer hydrophoben pyrogenen Kieselsäure zu bilden, und (B) In-Berührung-Bringen der wässrigen Suspension der hydrophoben pyrogenen Kieselsäure aus (A) mit einem nicht wassermischbaren organischen Lösungsmittel in einem Lösungsmittel zu Kieselsäure Gewichtsverhältnis von größer als 0,1:1, um dabei Abtrennung der hydrophoben pyrogenen Kieselsäure aus der wässrigen Suspension durch die Bildung einer Aggregation von hydrophoben Kieselsäureteilchen, die nicht wassermischbares organisches Lösungsmittel einschließen, in eine nicht wassermischbare organische Lösungsmittelphase zu bewirken.

2. Verfahren nach Anspruch 1, wobei die pyrogene Kieselsäure eine BET-Oberfläche von größer als 50 $m^2/g$ aufweist.

3. Verfahren nach Anspruch 1 oder 2, wobei die wässrige Suspension aus Schritt (A) ferner ein wassermischbares organisches Lösungsmittel in einer Menge enthält, die ausreichend ist, um Reaktion der pyrogenen Kieselsäure mit der Organosiliciumverbindung zu erleichtern.

4. Verfahren nach einem der Ansprüche 1 bis 3, wobei die pyrogene Kieselsäure durch Dampfphasen-Hydrolyse eines Halogensilans hergestellt ist.

5. Verfahren nach einem der Ansprüche 1 bis 4, wobei die Konzentration der pyrogenen Kieselsäure in der wässrigen Suspension innerhalb eines Bereichs von 5 bis 90 Gew.-% liegt.

6. Verfahren nach einem der Ansprüche 1 bis 5, wobei die katalytische Menge der Säure einen pH von 6 oder weniger während des In-Berührung-Bringens in Schritt (A) gewährleistet.

7. Verfahren nach einem der Ansprüche 1 bis 6, wobei das In-Berührung-Bringen in Schritt (A) bei einer Temperatur innerhalb eines Bereichs von 20°C bis 250°C bewirkt wird.

8. Verfahren nach einem der Ansprüche 3 bis 7, wobei das wassermischbare organische Lösungsmittel mindestens 10 Gew.-% der wässrigen Suspension ausmacht.

9. Verfahren nach einem der Ansprüche 1 bis 8, wobei das In-Berührung-Bringen in Schritt (A) in Gegenwart einer oberflächenaktiven Substanz durchgeführt wird, die die Reaktion der Organosiliciumverbindung mit der pyrogenen Kieselsäure erleichtert.

10. Verfahren nach einem der Ansprüche 1 bis 9, wobei die Organosiliciumverbindung in einer Menge zugegeben wird, so dass mindestens 0,04 Organosilyleinheiten pro $SiO_2$-Einheit in der pyrogenen Kieselsäure vorhanden sind.

Revendications

1. Procédé servant à préparer une silice fumée hydrophobe comprenant (A) de mettre en contact une suspension aqueuse d'une silice fumée avec (1) une quantité catalytique d'un acide et (2) un composé organosilicié choisi dans le groupe constitué d'organosilanes décrits par les formules $R^1_aH_bSiX_{4-a-b}$ (1), $R^2_nSiO_{(4-n)/2}$ (2) et $(R^3_3Si)_2NH$ (3) où chaque $R^1$ est un radical d'un hydrocarbure choisi de façon indépendante des autres comprenant 1 à 12 atomes de carbone, chaque $R^2$ est choisi de façon indépendante des autres dans le groupe constitué des atomes d'hydrogène ou de chlore et de l'hydroxy ou de radicaux d'hydrocarbures comprenant 1 à 12 atomes de carbone, à condition qu'au moins 50 pourcent en moles des substituants $R^2$ soient des radicaux d'hydrocarbures, chaque $R^3$ est choisi de façon indépendante des autres dans le groupe constitué du chlore, de l'hydroxy et de radicaux d'hydrocarbures comprenant 1 à 12 atomes de carbone, à condition qu'au moins 50 pourcent en moles des substituants $R^3$ soient des radicaux d'hydrocarbures, chaque X est choisi de façon indépendante des autres dans le groupe constitué d'atomes d'halogène, de radicaux alcoxy comprenant 1 à 12 atomes de carbone et de radicaux acyloxy comprenant 1 à 12 atomes de carbone, a = 1, 2 ou 3 ; b = 0 ou 1 ; a + b = 1, 2 ou 3, à condition que lorsque b = 1 alors a + b = 2 ou 3 ; et n est un nombre entier allant de 2 à 3 inclus, pour former une suspension aqueuse d'une silice fumée hydrophobe ; et (B) de mettre en contact la suspension aqueuse de la silice fumée hydrophobe de (A) avec un solvant organique non miscible avec l'eau avec une proportion en poids de solvant par rapport à la silice supérieure à 0,1:1 pour effectuer de cette manière la séparation de la silice fumée hydrophobe de la suspension aqueuse au moyen de la formation d'une agrégation de particules de silice hydrophobe, incorporant du solvant organique non miscible avec l'eau, dans une phase de solvant organique non miscible avec l'eau.

2. Procédé selon la revendication 1 dans lequel la silice fumée a une surface spécifique BET supérieure à 50 $m^2/g$.

3. Procédé selon les revendications 1 ou 2 dans lequel la suspension aqueuse de l'étape (A) comprend en plus un solvant organique miscible avec l'eau en quantité suffisante pour faciliter la réaction de la silice fumée avec le composé organosilicié.

4. Procédé selon l'une quelconque des revendications 1 à 3 dans lequel la silice fumée est préparée par l'hydrolyse en phase vapeur d'un halosilane.

5. Procédé selon l'une quelconque des revendications 1 à 4 dans lequel la concentration de la silice fumée dans la suspension aqueuse est comprise dans un intervalle allant de 5 à 90 pourcent en poids.

6. Procédé selon l'une quelconque des revendications 1 à 5 dans lequel la quantité catalytique de l'acide fournit un pH inférieur ou égal à 6 au cours de la mise en contact de l'étape (A).

7. Procédé selon l'une quelconque des revendications 1 à 6 dans lequel la mise en contact de l'étape (A) est effectuée à une température comprise dans un intervalle allant de 20°C à 250°C.

8. Procédé selon l'une quelconque des revendications 3 à 7 dans lequel le solvant organique miscible avec l'eau constitue au moins 10 pourcent en poids de la suspension aqueuse.

9. Procédé selon l'une quelconque des revendications 1 à 8 dans lequel la mise en contact de l'étape (A) est effectuée en présence d'un tensioactif qui facilite la réaction du composé organosilicié avec la silice fumée.

10. Procédé selon l'une quelconque des revendications 1 à 9 dans lequel le composé organosilicié est ajouté en quantité telle qu'il y a au moins 0,04 unité organosilyle pour une unité $SiO_2$ présente dans la silice fumée.